In situ Polymerization of Polyaniline in Wood Veneers

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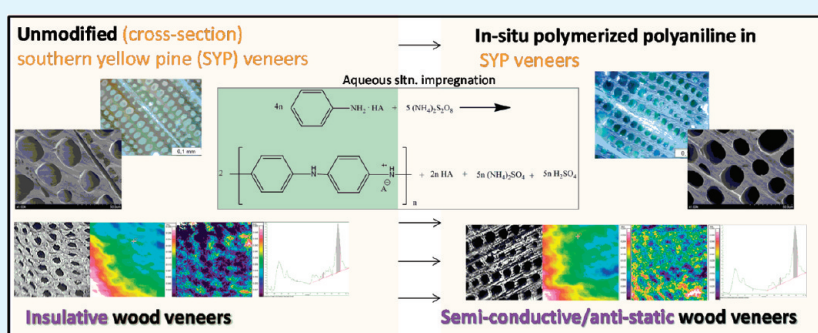
ABSTRACT: The present study describes the possibility to polymerize aniline within wood veneers to obtain a semi-conducting material with solid wood acting as the base template. It was determined that it is possible to synthesize the intrinsically conductive polymer (ICP) polyaniline in situ within the wood structure of Southern yellow pine veneers, combining the strength of the natural wood structure with the conductivity of the impregnated polymer. It was found that polyaniline is uniformly dispersed within the wood structure by light microscopy and FT-IR imaging. A weight percent gain in the range of 3−12 wt % was obtained with a preferential formation in the wood structure and cell wall, rather than in the lumen. The modified wood was found to be less hydrophilic with the addition of phosphate doped polyaniline as observed by equilibrium water swelling studies. While wood itself is insulating, the modified veneers had conductivities of 1×10^{-4} to 1×10^{-9} S cm^{-1}, demonstrating the ability to tune the conductivity and allowing for materials with a wide range of applications, from anti-static to charge-dispersing materials. Furthermore, the modified veneers had lower total and peak heat releases, as determined by cone calorimetry, because of the char properties of the ICP. This is of interest if these materials are to be used in building and furniture applications where flame retardance is of importance.

KEYWORDS: wood modification, conductive polymer, polyaniline, impregnation, fire retardance

■ INTRODUCTION

Interest in intrinsically conducting materials has been prolific in the past few decades with the most recognition of the area being the 2000 Nobel Prize in chemistry for the development of conductive polymers awarded to Heeger, MacDiarmid, and Shirakawa.[1,2] Traditional metals are inferior in terms of their mechanical properties and conductivity, while required high loading leads to heavier and inflexible systems. Carbon fillers have the disadvantage of having relatively poor conductivity and cannot be used in colored products.[3] Among the numerous conducting polymers such as polypyrrole, polyacetylene, and polythiophene, polyaniline is most often studied because of its lower cost, ease and control of synthesis, environmental stability, high electrical conductivity, and ease of blending with other polymers.[4] These conductive polymers contain conjugated double bonds, but are insulators unless they are oxidized, for example with protic acids. This doping of the

polymer and this protonation degree can be tuned in order to steer the degree of conductivity of the material.[5] Regarding polyaniline, the level of conductivity when fully doped is around 1×10^{-2} to 100 S cm^{-1}.[6] This tunability of the characteristics makes polyaniline of interest in many different applications including electronic devices, batteries, solar cells, electromagnetic radiation, anti-static materials, electric heaters, and even filtration of heavy metals.[7,8]

Conductive materials can be broken down into 3 different categories with increasing conductivity. The first is insulating materials including most thermosets and wood materials in the range of 1×10^{-16} to 1×10^{-12} S cm^{-1}, which are typically used for, for example, wire coatings. However, these materials can

build up and hold onto static electrical charge that can deliver an uncomfortable and in some cases dangerous shock or electrical spark. The second category includes dissipative or anti-static materials with conductivities in the range of 1×10^{-11} to 1×10^{-9} S cm^{-1}, which allow movement of electrons from higher to lower charge densities, inhibiting the delivery of a spark or shock. Often, to obtain this, migrating additives are formulated into thermoplastics. This is a feasible solution; however, this can result in contamination and aesthetic issues such as "blooming" or appearance of the small molecule aggregating on the surface. The third category includes moderate-highly conductive "shielding" thermoplastic materials used for, for example, shielding of electromagnetic radiation, and have conductivity values of 1×10^{-9} to 1×10^{-1} S cm−. To achieve this level of conductivity with a polymer-based system, we must add large amounts of carbon or metal particles/fibers, which detrimentally effects the impact and elongation while an increased chance of particle loss (or sloughing) from the material is likely.[9]

Because of the poor mechanical properties of ICPs, along with the difficulty in dissolving or melting them, they have often been combined with traditional thermoplastics such as a polyethylene terephthalate and polyethylene to obtain a suitable balance between conductivity and mechanical performance.[10] It has been shown that by varying the dopant, and selecting from a wide range of protic acids, a large effect on the conductivity, thermal stability, processability, and adsorption can be achieved.[11−15]

An increasingly important group of materials that has obtained a significantly increased interest during the last decade are those based on renewable resources.[16] Within this group, wood-based materials play a key role because of availability and suitable material performance in many respects. For example, wood is an excellent composite material with very good mechanical performance in relation to its weight.[17] Wood, however, also suffers from some limitations such as dimensional changes with water content, poor fire resistance, and susceptibility to biological degradation.[18] Therefore, wood is often modified or protected by coatings to reduce the effect of these drawbacks. One example is the impregnation of hydrophilic monomers in the cell wall structures with subsequent immobilization via polymerization in the cell wall to obtain a more dimensionally stable material.[19]

To further utilize renewable materials, increase mechanical properties, and reduce cost, wood components including sulfonated lignin, cellulose, and saw dust have all been coated with polyaniline and conductive composites made from these particles or cellulose fibers.[20−25] Previous research, involving the coating of wood sawdust with polyaniline, has demonstrated that polyaniline coatings on wood and cellulose fibers can lead to increased fire retardancy.[26,27] However, impregnating an aniline monomer solution into wood and synthesizing polyaniline in-situ, in order to take advantage of the complex and robust structure of wood itself, has received less attention.

The aim of this project is to use the complex structure of wood as a renewable material that is by nature a light yet strong material and modify with intrinsically conductive polymers in order to obtain a novel functional material. The proposed advantage is not only to obtain a conducting material but also to address other important restrictions for wood such as the effect of modification on the dimensional stability, strength, fire resistance, and morphology of the conductive polymer within the architecture of the wood structure.

2. EXPERIMENTAL SECTION

2.1. Materials. The crown cut/flat cut Southern Yellow Pine (Carolina pine) veneer was received from Specialised Veneers Ltd., Aylesburg, United Kingdom. After conditioning at 65% RH, the veneers had approximately 11 wt % moisture content and a density of 530 kg/m^3. The aniline (≥99.5% purity), phosphoric acid (85 wt % in H$_2$0, 99.9% trace metal basis), sulphuric acid (95-98%), dodecylbenzenesulfonic acid sodium salt, and ammonium peroxydisulfate (APS) (≥98%) were all used as received from Sigma Aldrich.

2.2. Method and Procedures. *Impregnation/Polymerization Procedure.* The veneers were cut to $0.6 \times 5.0 \times 5.0$ mm^3 and in sets of 5 were vacuum pressure impregnated for 24 h at 10 bars under inert atmosphere. The first hour, the solutions were kept at 0 °C and then room temperature for the remaining time, with solution of aniline in water at concentrations of 0.20, 0.10, and 0.05 M, phosphoric acid (PA) (sulfuric acid (SA), or n-dodecylbenzenesulfonic acid (DBSA)) with (dopant)/aniline molar ratio of 1 and APS/aniline ratio of 1.25. These reactant ratios have been found to result in the emeraldine salt form of polyaniline with 50% of the emeraldine base protonated or oxidized.[11] (Figure 1.) The polyaniline synthesized from this
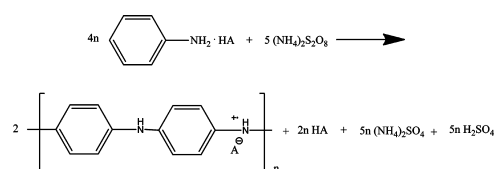

Figure 1. Reaction scheme of 50% oxidized polyaniline.

recipe under these conditions have been characterized extensively and the molecular weight reported to be 75−95 kDa.[28] The samples were then dried in a vacuum oven at 50 °C for 48 h. The polyaniline particles formed in the solution containing the wood veneers and after 48 h, the modified veneers were removed and the liquid was decanted, yielding the particles that were dried for 48 h at 50 °C in order to be tested further.

2.3. Weight Percent Gain (WPG), Dimensional Stability, Equilibrium Moisture Content, and Leaching Evaluation. The samples were first conditioned at 65% RH before impregnation, with weight and dimensions measured with a slide caliper at midpoints of the sample. The weight and dimensions were then measured directly after being taken out of the impregnation solution, and after drying the impregnated samples. This allowed for calculation of the uptake of the impregnation solution, weight percent gain (WPG) of the polymer, bulking or volume swelling from polymer uptake, moisture weight gain, and water swelling of the veneers. For a more in-depth description, refer to previously published work.[29]

Leaching studies were done according to the EN-84 standard over 14 days. The weight loss after 14 days in water and oven drying were taken gravimetrically.

2.4. ^{1}H-NMR (of leachate). NMR analyses were performed on a Bruker AM 400 utilizing deuterated chloroform containing 1 vol % TMS as an internal standard. 1 g of the modified veneer samples were soaked in 5 ml of deuterated water for 92 h and then the solvent was analyzed for extractives.

2.5. Resistance Measurements and Conductivity Determination. Modified veneers were cut of 0.5 cm thickness, l, and 3.0 cm diameter, d, and were placed tightly between two gold plate electrodes connected to a Solartron 1296 electrochemical interface coupled to a Solartron 1260 frequency response analyzer, and the impedance spectrum was measured with an AC amplitude of 10 mV and frequency range from 1 MHz to 0.1 Hz. The resistance at low frequency, R, was collected and analyzed by the SMaRT software, from Solartron Analytical. The conductivity, σ, was then calculated as $\sigma = (4l)/(\pi d^2 R)$.

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Table 1. Naming Scheme

| sample name	type of sample	aniline aqueous solution concentration (M)	type of dopant (protic acid) used
0 M unmod	unmodified veneer	0	none
0.05 PANI-PA	doped polymer modified veneer	0.05	phosphoric acid
0.1 PANI-PA	doped polymer modified veneer	0.10	phosphoric acid
0.2 PANI-PA	doped polymer modified veneer	0.20	phosphoric acid
0.2 PANI-ND	non-doped polymer modified veneer	0.20	none
0.1 PANI-SA	doped polymer modified veneer	0.10	sulphuric acid
0.1 PANI-DBSA	doped polymer modified veneer	0.10	n-dodecylbenzenesulfonic acid
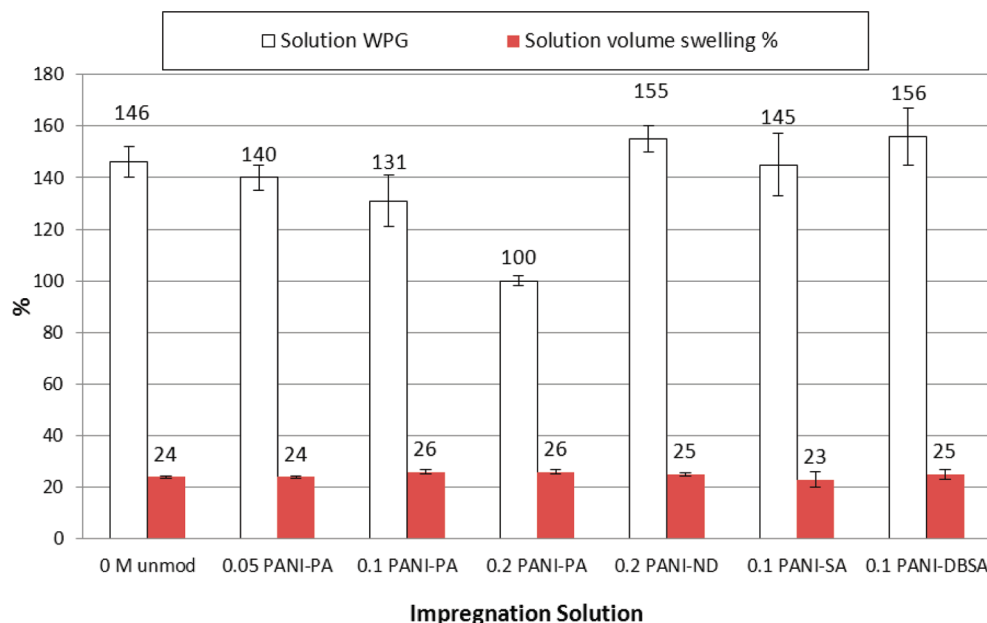
Figure 2. Gravimetric and volumetric determination of impregnation solution WPG and volume swelling.

To determine the conductivity level of the synthesized PANIs with different dopants separately, we pressed dried PANI powders under 5 tons pressure to make pellets of 0.15 cm thickness, l, and 1.28 cm diameter, d. The pellets were then placed in the measurement cell and analyzed as described above.

2.6. Laser Cutting Technique. The samples were ablated transverse to the fiber direction to give a cross section using a pulsing UV (KrF) exciplex laser (Lumonix 600LX) (43) with radiation emission of 248 nm. The irradiation energy was 375 mJ, the pulse width was 20 ns, and the pulse frequency was 3 Hz.

2.7. Optical Microscopy. An Olympus BX51 Optical microscope was used to observe cross-sections of the veneers. AnalySIS Five digital imaging solutions software was used.

2.8. Scanning Electron Microscope. The dry cross-sections were fixed to a metal stub using a carbon based puddy (LEIT-C-Plast from Ted Pella) and coated with a double layer coating (ca 5 nm) consisting of graphite and gold−palladium using Agar HR sputter coaters. A Hitachi S-4800 scanning electron microscope operated at 1 kV was used to capture secondary electron images of the surfaces.

2.9. Fire Retardancy Testing. Fire testing was performed according to ISO 5660 (Cone calorimeter) for ignitability and for rate of heat release. The irradiance used was 50 kW/m^2. For these tests the veneers were glued to gypsum plasterboards. The average value was reported from a minimum of three repeats.

2.10. FT-IR Imaging. The FT-IR images were recorded in attenuated total reflectance mode on a Spectrum Spotlight 400 FT-IR microscope connected to a Spectrum 100 FT-IR spectrometer (PerkinElmer Inc.). The area of interest was first captured by a CCD camera and then scanning of the area was performed in imaging mode by a 16 point dual array liquid N$_2$ cooled MCT detector. Samples were moved stepwise in the x- and y-direction resulting in the assembly of a chemical image of the pre-defined area. The

measurement provided a pixel resolution of 6.25 × 6.25 μm^2. The FT-IR spectra were recorded in 8 cm^{-1} spectral resolution, zero filling factor 1, between 4000 and 720 cm^{-1}. 16 scans per pixel were averaged to increase the signal to noise ratio.

Image areas were taken on cross sections that had been cut by laser ablation. Care was taken to avoid ray cells or resin channels, although this was a factor in poor sample contact in some cases.

The output of IR-imaging microscopy is a pseudo-color FT-IR absorbance image calculated from the average absorbance of the whole IR range after atmospheric compensation.[30]

3. RESULTS AND DISCUSSION

The aim of the study was to determine if veneers could be impregnated with aniline aqueous solution in order to in-situ polymerize polyaniline in the structure of wood veneers in order to combine the properties of conductive polymers with the complex lightweight yet strong structure of wood.

A key question is how the water-soluble monomer interacts with the wood structure. It is also of interest to determine whether the water insoluble polymer will precipitate throughout the wood structure or only in the lumen.

3.1. Modification Process. The impregnation/polymerization was performed according to a batch-wise process. The veneer samples were placed in a 1 L autoclave, weighted down, and vacuum was used for 30 minutes in order to pull out all of the air in the hollow wood structure, to allow better impregnation of the added monomer solution.

To achieve better impregnation, the soft wood, southern yellow pine, sap wood was chosen because of its known ease of
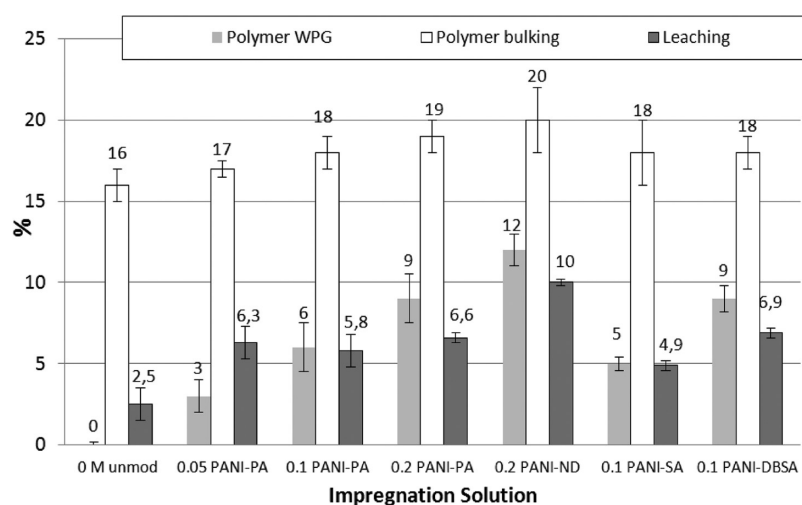
Figure 3. Gravimetric and volumetric determination of polymer WPG, bulking, and leaching.

ability to impregnate as the pores within the structure remain open after drying in contrast to hardwoods.

The aniline solution components were chilled to 0 °C, mixed, added to the veneers under pressure and the metal autoclave kept in an ice bath for 1 h. This reduced temperature greatly slows the reaction time and exothermicity and further has been shown to increase the conductivity of the formed polyaniline. This low temperature should also aid in allowing the monomer solution time to penetrate the wood structure, before reacting to higher molecular weights and increasing degrees of hydrophobicity and insolubility.

The aniline aqueous solution concentration varied from 0.05 to 0.20 M in order to determine if the amount of polymer in the system will significantly affect the conductivity and to investigate if there is a minimum concentration needed for conductivity. These concentrations were chosen because this is similar to what has been investigated in other work.[20] Further, the maximum concentration was 0.20 M because this is where the solution begins to reach saturation of the salt formed by the combination of the aniline (behaving as a base) and the protic acid. The dopant was altered to determine the effect of pKa and size on penetration into the wood structure, and the effects on the wood properties.

3.2. Impregnation Efficiency, Solution Weight Percent Gain (WPG), and Bulking (Volume Swelling). First, the pine veneers were vacuum pressure impregnated with a solution of aniline, dopant, and APS, and left for 24 h under pressure. A large amount of polyaniline particles formed outside of the wood in the autoclave, whereas the wood veneers appeared different degrees of dark green depending on the concentration. The wood samples were removed from the autoclave, the veneer exteriors were washed free of excess particles with water and acetone, and then blotted dry. The dimensions and weight were measured to determine the degree of solution uptake and swelling. It can be observed in Figure 2 that the solution weight percent gain (WPG) of the veneers decreases with increasing phosphate polyaniline solution concentration. This trend is not observed with the non-doped and SA- and DBSA-doped solutions, in which it seems that a more favorable interaction with the wood and the solution is observed. However, no significant effect can be determined by this method regarding volume swelling, perhaps

because of the small dimensions and too minor changes to be detected.

3.3. Impregnation Efficiency–Polymer Uptake, Weight Percent Gain (WPG). Once the impregnated veneers were vacuum dried, the weights and dimensions were measured again to determine the polymer WPG and bulking respectively. (Figure 3) For the PANI-PA (phosphorous doped) samples, the polymer WPG increased proportionally to the solution concentration from 3, 6, and 9 wt % for concentrations of 0.05, 0.10, and 0.20 M, respectively. The dopant also had an effect on the amount of polymer that is taken up by the wood WPG. 0.1 PANI-SA took up similar amounts in comparison to 0.1 PANI-PA, but PANI-DBSA polymer WPG was almost double this amount. This could be due to the more bulky chains of DBSA that were able to better adsorb to the wood structure or due to the higher viscosity of the DBSA solution that was observed.

3.4. Impregnation Efficiency–Polymer Uptake, Cell Wall Bulking. Polymer bulking was determined by comparing the dimensions of the dry veneers before and after impregnation. It should be noted that even unmodified veneers (0 M PANI-PA or 0 M unmod) had a more expanded structure after the water vacuum pressure impregnation and drying. It can be observed that the increasing concentration corresponds with the increase in volume of the veneers, with the exception of the non-doped 0.2 PANI-ND samples in which significant volume swelling was observed. This is an indication of cell wall bulking, since if the polymer was to only form in the lumen, no volume swelling would be observed. It appears that even at higher concentrations, the aniline solution was able to polymerize in the cell walls, as indicated by this cell wall bulking, but that the non-doped sample was able to fill the cell wall most efficiently. This is hypothesized to be due to the slower reaction rate and exotherm without the addition of the protic acid, allowing for more time for the chains to swell the cell wall. It is also possible that smaller chains were formed without the protic acid and that is why more leaching was observed from 0.2 PANI-ND.

3.5. Polymer Immobilization Determined by Leaching Studies. Five of the veneers were then placed in water for 14 days and the water was changed daily according to the EN-84 standard. (Figure 3) After 14 days the samples were vacuum dried and the weight loss was compared to the dry weight before leaching. It is observed that the weight loss after leaching
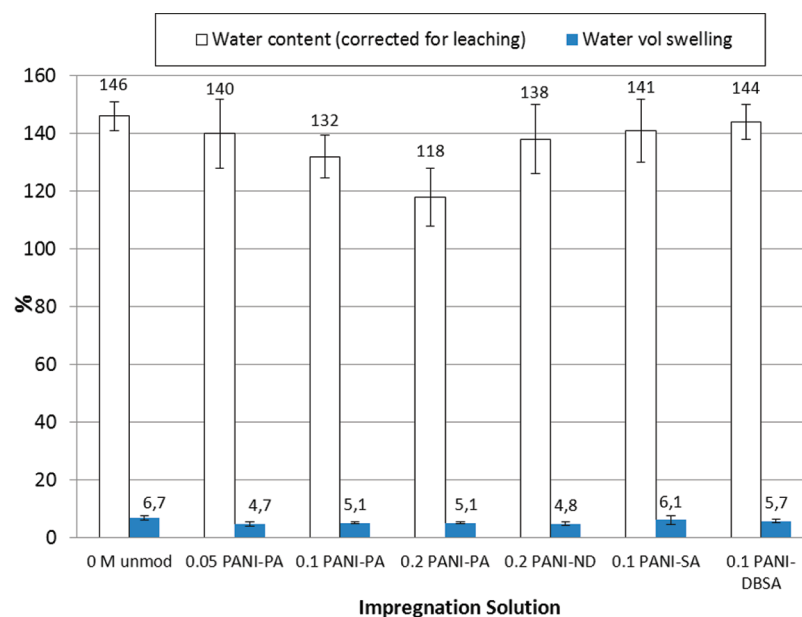
Figure 4. Weight of water uptake of the modified wood samples and amount of volumetric swelling or bulking in water after 14 days according to EN-84 standard.
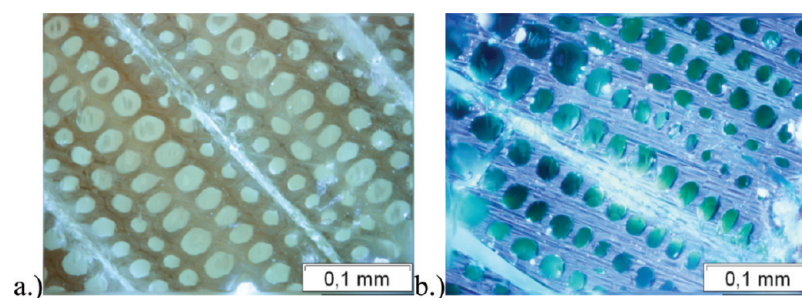

Figure 5. Light microscopy images of the cross-section of (a) unmodified vs (b) 0.2 PANI-PA unleached veneers.

in water for 14 days is significant relative to the polymer WPG. Nevertheless, a large degree of conductivity remains despite this very efficient leaching treatment. Further, there is no color change of the veneers observed and they remain dark green. This indicates that a fraction of the leachable compounds comes from the wood itself, possibly due to acid hydrolysis or from the other biproducts formed during the polyaniline reaction such as ammonium sulphate and hydrogen sulphate. The leaching from the modified veneers is also fairly consistent from 5−6 wt % regardless of aniline concentration, with the exception of the 0.2 PANI-ND (nondoped polyaniline).

3.6. Leachate Characterization. Analysis of the leachate of the 0.2 PANI-PA solution by proton NMR shows peaks at 6.8, 7.9, 8.2, and at 9.2 ppm indicating the presence of 2-furaldehyde and formic acid, the degradation products of hemicelluloses glucose and xylose that have been hydrolysed by the strongly acidic monomer solution.[31] When the veneers were soaked in a sulphuric acid aqueous solution of pH 2, leached in water for 14 days, and measured, the result was only 3.3 ± 0.5 wt % loss. This is only slightly higher than the weight loss of the 0 M unmod veneer that had been impregnated with water at pH 7. This indicates that a small amount, though not all, of the weight loss is a result of the lower pH of the treatment.

3.7. Equilibrium Water Uptake. By swelling the modified samples in water for 14 days with the EN-84 standard, the uptake of water of the modified veneers in comparison to the unmodified veneers was measured (Figure 4). All treatments with ICPs decreased the equilibrium water uptake of the samples, with impregnation solution concentration correlating to a reduction in water uptake. This indicates that more polyaniline has bulked the cell wall in the case of the 0.20 PANI-PA in comparison to the lower concentrations. Although there is a slight reduction in water uptake with the 0.2 PANI-ND, there is no significant effect with the other dopants, SA and DBSA, which indicates that the polyaniline formed and doped with these compounds did not bulk the cell wall as effectively. This could be contributed to the fact that sulfonic acid doped polyaniline has been observed to be more hydrophobic in nature compared to the phosphorous-doped polyaniline. This increased hydrophobicity was also observed with non-doped polyaniline in comparison to phosphorous doped.[32] DBSA-doped polyaniline could be too bulky and hydrophobic to effectively bulk the cell wall. The phosphorous-doped PANI appears to provide for the least amount of water uptake, whereas the other dopants, SA and DBSA, are similar to the unmodified wood after correcting for the leached weight. The volume swelling of the modified samples also appears to follow this trend, with the SA and DBSA doped polyaniline veneers having more volume swelling in water compared to the phosphorous and non-doped polyaniline modified veneers.
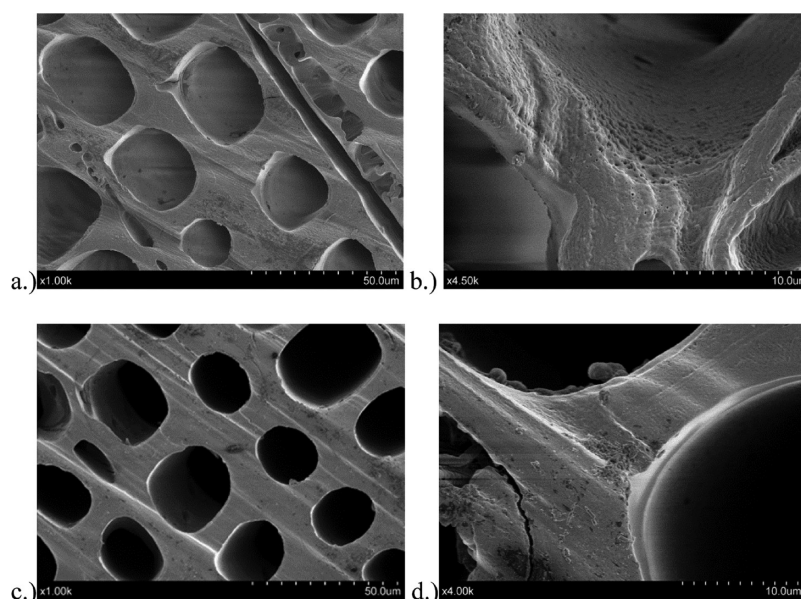
Figure 6. SEM images of the cross-section of (a, b) unmodified vs (c, d) 0.2 PANI-PA unleached veneers.
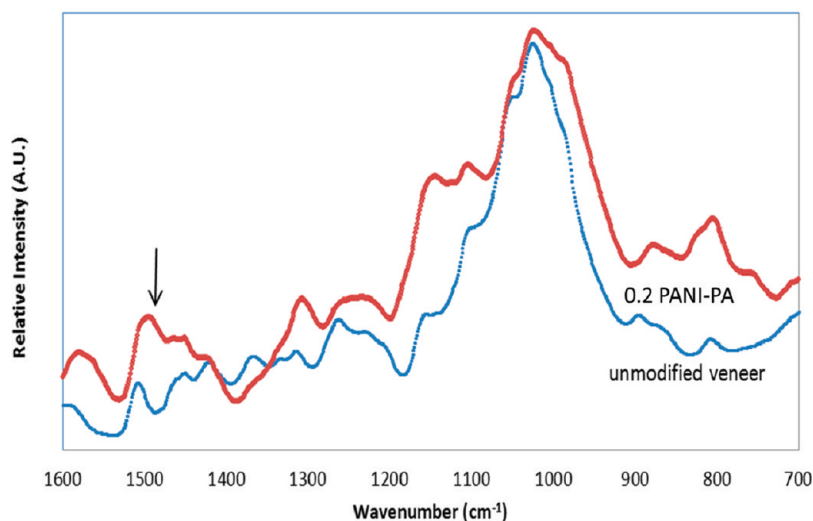

Figure 7. FT-IR spectra of unmodified and 0.2 PANI-PA veneer.

3.8. Location and Appearance of the Polymer in the Modified Wood. To locate the polyaniline formation in the veneer structure or wood anatomy, the veneers were cross-sectioned by cold laser ablation and imaged by light microscopy. Interestingly, it was observed that the formation of polyaniline did not occur to a large extent in the lumen, which was observed to remain clear of polymer (Figure 5). Because every wood cell lumen is like a miniature reactor of empty space, it was expected that a large amount of polymer would also grow off of the lumen walls similar to the large number of PANI particles that was observed in the autoclave around the wood samples. This was observed to a small degree, but not to the extent that was expected. This is most likely due to the fact that this was an aqueous aniline solution in which a large volume fraction is water. The polyaniline is highly colored due to the conjugated structure and all of the samples, regardless of the concentration, appear black with blue and green metallic hues. It is interesting to note that the polymer appears homogeneously distributed throughout the network structure of the wood.

To determine if polyaniline could be identified in, or adsorbed on, the wood structure, we utilized SEM to image the laser ablated cross section of the untreated and 0.2 PANI-PA unleached veneer (Figure 6). It was observed that in the unmodified veneer, that there are little to no particles observed in the less magnified samples (Figure 6a) and that the porous structure of the cell wall can clearly be discerned (Figure 6b). However, in the modified sample, dark specks can be observed in the network, with agglomerates dispersed throughout the structure in the less magnified image (Figure 6c). The particles are clearly observed to be adhered to the cell wall in the more magnified image (Figure 6d). Overall, a surprisingly small amount of particles are observed adhering to the lumen.

In an effort to determine the location of polyaniline in the network structure, FT-IR imaging was used to image the cross sections of unmodified and 0.2 PANI-PA unleached veneers. First FT-IR ATR spectra were taken of the unmodified and modified veneers in which the peak from the benzenoid ring of doped polyaniline is observed at 1480 cm^{-1} for the modified sample.[1] (Figure 7, indicated by an arrow) A visible image was
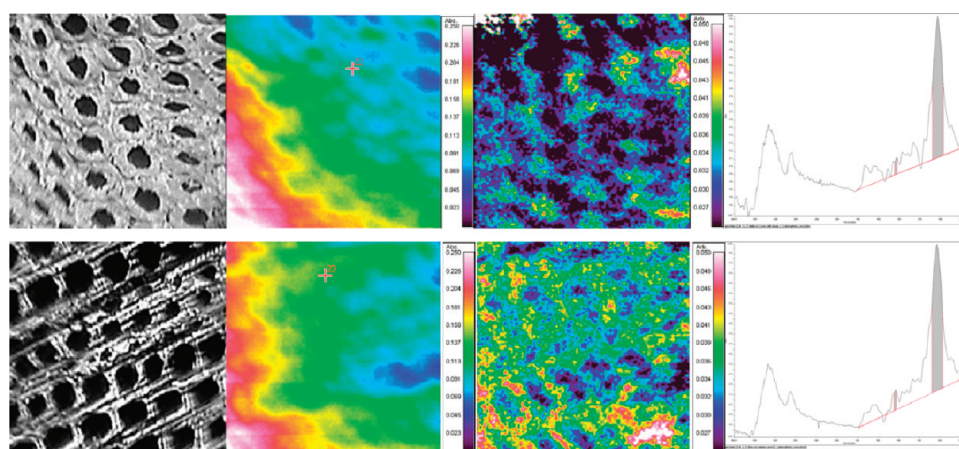
Figure 8. FT-IR imaging (each image 150 × 150 μm) of the cross-section of the unmodified veneer (top row) and 0.2 PANI-PA modified veneer (bottom row) with the visible image to the far left, the average absorbance second to the left, the band ratio image (1480:1080 cm^{-1}) second from the right, and the band ratio illustrated in the selected pectra to the far right.
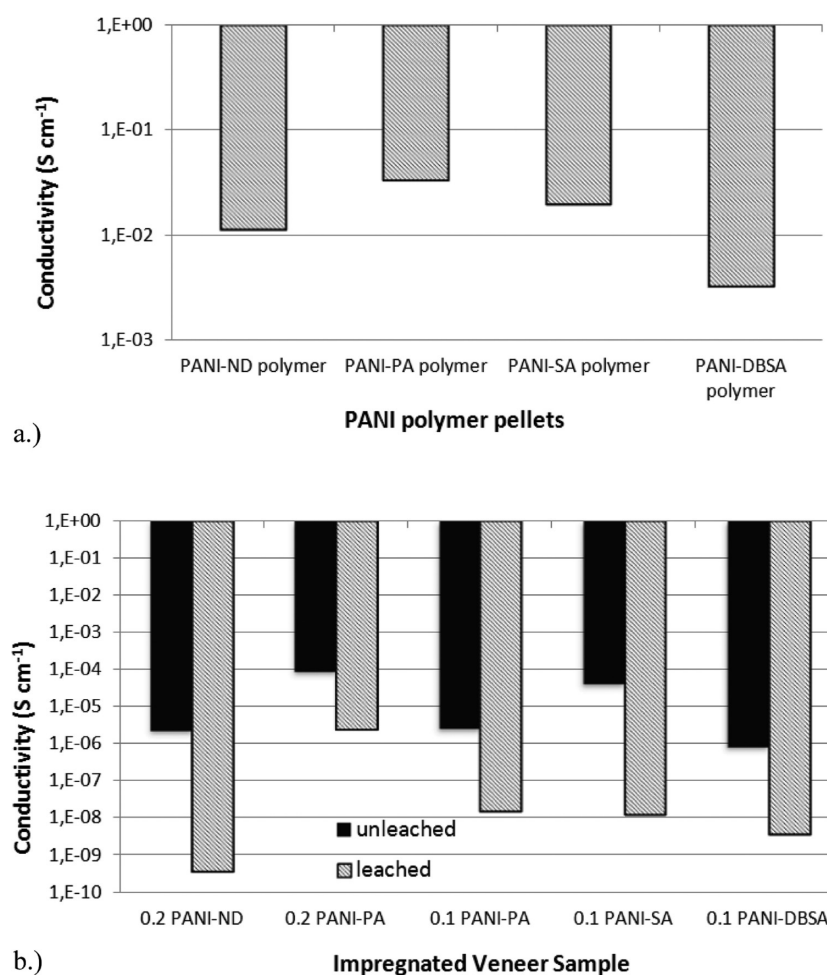

a.)

b.)

Figure 9. (a) Conductivity of non-doped and doped polyaniline powders, and (b) Conductivity of the in situ polymerized polyaniline in the modified veneers, as calculated from the resistance at low frequency measured by impedance spectroscopy.

then collected of each sample using FT-IR imaging and then a measurement of the area was taken of 150 × 150 μm.(Figure 8, farthest to the left) The average absorbance is the main data file collected, which shows good contact of the crystal with both samples (Figure 8, second to the left). The band ratio was then taken of the average absorbance at 1480 cm^{-1} to the peak at 1080-1040 cm^{-1} which is the signal from the vibrations of

glucomannan in wood that does not change with the addition of polyaniline.[33] (Figure 8, farthest to the right) This band ratio was then mapped to show the intensity of the peak at 1480–1500 cm^{-1} in order to determine the concentration and presence of polyaniline. (Figure 9, second from the right) It is clear that the intensity of this peak is higher for the polyaniline modified sample and that the polyaniline appears homogeneous
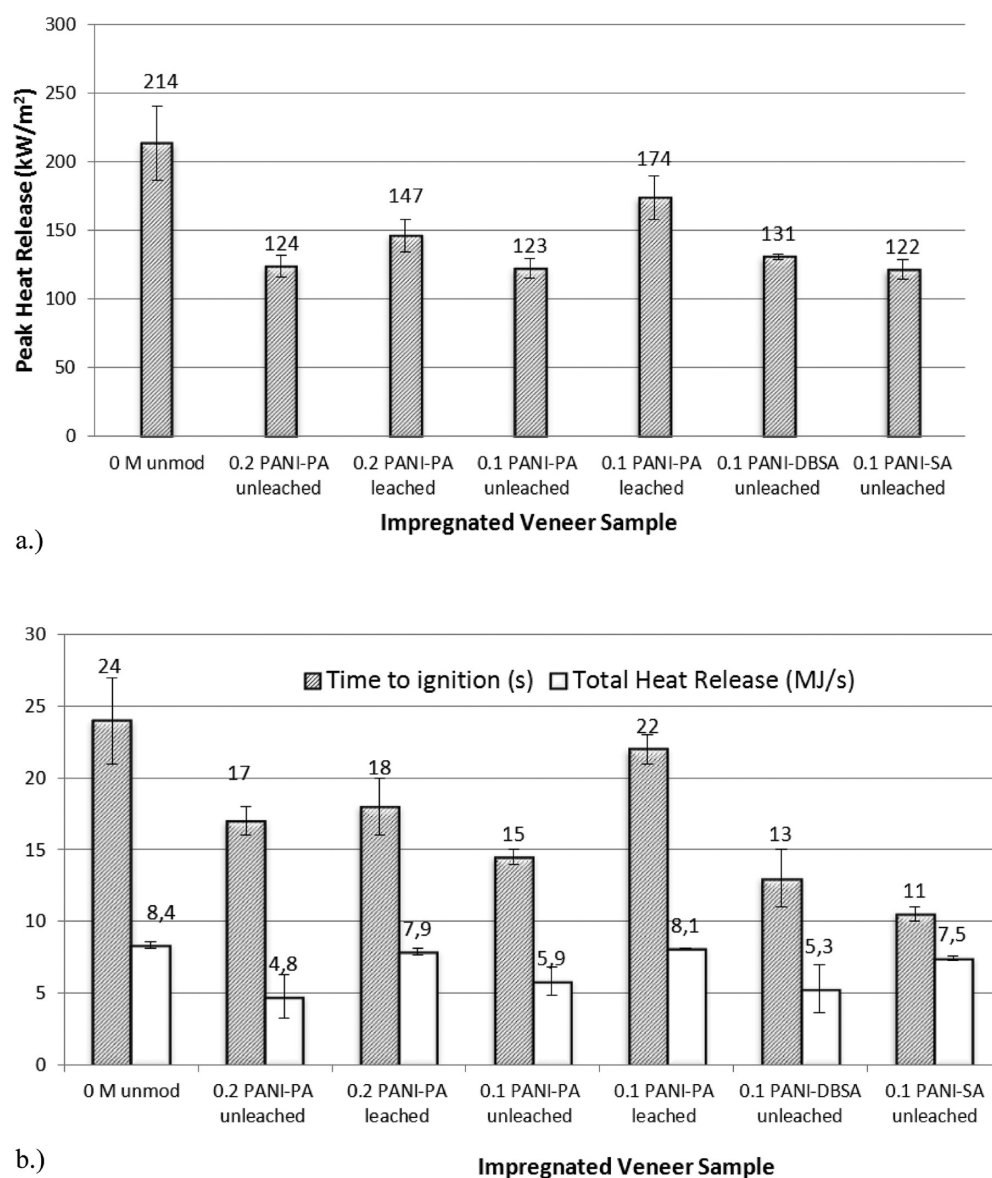
Figure 10. (a) Peak heat release and (b) time to ignition, and total heat release of unmofidied and selected modified samples, as measured by cone calorimetry.

in the structure with concentration being highest in the middle lamella.

3.9. Conductivity of the Polymers and Modified Wood. After establishing the location of the polyaniline formation in the modified veneers, a further objective is to determine if the addition of polyaniline could result in a semi-conductive wood material and if so what minimum concentration is needed to achieve this. Unmodified veneers and 0.05 PANI-PA veneers were insulating materials and are therefore not presented in Figure 9. The wood−polyaniline composites have a degree of semi-conductivity that is not as conductive as polyaniline alone, but that is comparable to traditional commercial antistatic materials. This is promising because, even with these preliminary results, with a WPG of less than 10 wt %, these conductivity results indicate that aniline goes into the cell wall and polymerizes in the wood connective network and not just within the lumen voids. If there were polymerization only in the lumen, the polymer would be isolated into closed cells, preventing the connective network

needed to result in a conductive material. It is of note that even the polyaniline polymer pellet sample, not containing a protic acid, shows semi-conductive properties. This is likely due to the fact that the particles were formed in the same autoclave solution containing the wood veneers. It has been previously demonstrated that aqueous solutions containing wood are acidic (pH between 4.5−5), with a pH of even lower levels within the fiber walls,[34] which is the ideal pH for the protonation of polyaniline and for the emeraldine salt to form without the addition of a protic acid.[35] Even the veneer impregnated with this non-doped aniline mixture shows a degree of semi-conductivity which is even higher than the 0.1 PANI-DBSA veneer (2.3×10^{-6} S cm^{-1} compared to 8.5×10^{-7} S cm^{-1}, respectively). This is appealing because the harsh conditions of the low pH created with the addition of a protic acid may not be necessary. However, the leaching produced a large drop in the conductivity of 0.2 PANI-ND in comparison to 0.2 PANI-PA. In summary, the large range of conductivities,

from 1×10^{-4} to 1×10^{-9}, shows that this method is an ideal way to tune the conductivity properties.

3.10. Fire Retardation Properties of Modified Veneers.

It has been found in the past that polyaniline in sawdust composites has resulted in charring instead of burning.[27] Although it is not the main objective in this study, if these composite materials are of interest as components in building materials, it is of interest to characterize their fire sensitivity. It is also of interest to determine if the other dopants used in this study, besides phosphorous, could give protection against fire. In analysis of the samples by cone calorimetry (Figure 10), it was observed that addition of polyaniline greatly reduced the peak heat release (Figure 10a) and the total heat release values (Figure 10b). This is largely due to the charring of the ICP that inhibited the immediate combustion of the wood. For purposes of simplicity, only selected samples have been tested to get an idea of how the doped polyaniline affects the fire retardance. The 0.2 PANI-ND and the leached samples of PANI-DBSA and PANI-SA have not been tested. After leaching, the 0.20 M phosphorous-doped polyaniline impregnated sample was not significantly affected while the sample impregnated with 0.10 M phosphorous-doped polyaniline performed poorly. The total heat release was lowest for the phosphorous and DBSA-doped 0.1 M polyaniline unleached samples, whereas the sulfuric acid-doped 0.1 M polyaniline unleached sample was less effective in reducing the heat release (Figure 10b). The time to ignition was actually faster for treated samples, which could be due to the much lower hydrophilicity of the samples, and/or due to the trace amount of byproducts from the polymerization in the system. This is confirmed by the increased time to ignition of those samples that were leached in water over 14 days (Figure 10b).

4. CONCLUSIONS

It was found in this study that it is indeed possible to polymerize polyaniline in wood veneer structures. The concept of using a water-soluble monomer with the ability to penetrate the wood cell wall and polymerize in situ, forming a water insoluble polymer that is retained in the wood structure has been demonstrated. Furthermore, this results in a connective ICP netowork, that allows for fabrication of wood based semi-conductive materials. These modified veneers were found to have weight percent gains from 3−12 wt % and bulking of the cell wall was observed from volume swelling, indicating polymerization of polyaniline in the cell wall. The phosphorous-doped polyaniline modified veneers were observed to have more hydrophobic character as observed by equilibrium water swelling studies. The location of the polyaniline was found to be not in the lumen, but homogeneously distributed in the wood network structure as determined by light microscopy, SEM, and FT-IR imaging. The veneers were found to be semi-conductive in comparison to the unmodified insulative materials and had a wide range of tunability depending on the concentration and dopant of the ICP. This opens the door for a wide range of anti-static, dispersive, and semi-conductive materials that are cheaper because they are largely made of wood, yet have structural strength and are lightweight because of the high degree of porosity when compared to current ICP filled composites.

Further, the modified veneers showed a further advantage of having fire retardant properties in terms of lower heat total and peak heat release when burning. This is especially of interest if these materials are to have future application in building materials and furniture. However a disadvantage of this was that the time to ignition was faster as determined by cone calorimetry.

Future work in this area could include investigating how to increase the conductivity of the semi-conductive veneers. Some initial ideas could include different methods to open up the structure of the wood, such as the use of microwaves to determine if this increases the conductivity. Other efforts could include trying to increase the aniline solution concentration by altering solvents and conditions. Additionally, other conductive polymers that are less widely studied and that may provide better bulking of the cell wall and greater conductivities could be studied. More research on polyaniline impregnation of wood could involve the modification of wood with hydrophobic PANI, by altering the dopant chemistry such as use of alkyl phosphonic acids. It could also be attempted to modify larger dimensions of wood and investigate any gradient effects. Further effects of polyaniline on mold and fungal durability could be investigated.

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Notes
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